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Corrosion Resistance Through the Application of Anti-Corrosion Coatings

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Additional information is available at the end of the chapter

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1. Introduction

Corrosion is the surface disintegration of metals/alloys within specific environment. Some metals basically exhibit high corrosion resistance than others and this can be attributed to several factors like their chemical constituents, the nature of electrochemical reactions itself and others. The corrosion resistance of metals can be defined in terms of its ability to withstand aggressive conditions. This determines to a large extent the operational lifetime of components in service. However, there are several definitions of corrosion and according to International Union of Pure and Applied Chemistry (IUPAC) "Corrosion is an irreversible interfacial reaction of a material (metal, ceramic, and polymer) with its environment which results in consumption of the material or in dissolution into the material of a component of the environment. Often, but not necessarily, corrosion results in effects detrimental to the usage of the material considered. Exclusively physical or mechanical processes such as melting or evaporation, abrasion or mechanical fracture are not included in the term corrosion" (Heusler *et al.*, 1989). It is realized that this definition virtually include all engineering materials and it is considered as a wide definition. Hence, another definition is given by ISO 8044-1986 which states inter-alia: "Physicochemical interaction between a metal and its environment which results in changes in the properties of the metal and which may often lead to impairment of the function of the metal, the environment, or the technical system of which these form a part". (EFC Working Party 7: Corrosion Education, 2012).

It is realized that the most widely used definition of corrosion is the degradation of material by its reaction with its environment (Trethewey and Chamberlain, 1995). The following are the main concepts in the definition: degradation, material, reaction, and environment. Generally, corrosion is conceived as harmful that is, the degradation/destruction that occurs with corrosion, however, it must be noted that there are numerous advantageous uses in

respect of corrosion. Degradation is regarded as the deleterious effects of corrosion and it greatly outweigh their usefulness. Materials are used by human being to achieve their technological prowess but of all the available ones, it is known that metals are “inter pares” among them. It was based on the fact that materials have good physical, mechanical, and chemical properties (Ige, 2007). It has also been observed that the term reaction is also being used in classifying corrosion based on their mechanism; hence it can be physical, chemical or electrochemical (Fontana, 1987; West, 1986). The most significant is the electromechanical reaction, which involves the transfer of electrons between the participants. Environment is described as all species adjacent to the corroding metal at the time of the reaction. Environments that cause corrosion are called corrosive and materials/metals that suffer corrosion are called corrodible (Trethewey and Chamberlain, 1995; West, 1986).

The factors that affect the environment include nature, thermodynamics and the kinetic among others (Ige, 2007) but generally, corrosion resistance or chemical resistance depends on many factors. Its complete and comprehensive study requires knowledge of several fields of scientific knowledge (Fontana, 1987). Some of these factors are as listed: effects of oxygen and oxidizers, temperature, velocity, corrosive concentration, galvanic coupling, metallurgical factors, (Wang, 2009; West, 1986; Tendayi, 2010).

Materials selection is a powerful tool for dealing with severe corrosion. Failures occurring as a result of corrosion attack can be very expensive therefore preventing or reducing these attacks becomes very significant to the industry and households (Fontana, 1987). The materials engineer’s solution to the fatal failure induced by corrosion is simply the fabrication of anti-corrosion coatings with superior chemical and mechanical properties than the parent material. The improvement of the lifespan and performance of metallic alloys and components through application of numerous anti-corrosion coatings is highly advantageous (Popoola *et al.*, 2012). These coatings enable more efficient metals/components, efficient industrial operations, cost reduction, saving of scarce material resources and reduction in pollutant emissions. Anti-corrosion coatings often involve development of new surface materials which can impart numerous functional properties unto the surfaces of metals/components. New materials include composites, nano-composites, nano-particles. Numerous industries make use of anti-corrosion coatings since almost all engineering materials (composite, alloys, metals, polymers and ceramics) can be used as reinforcement coating on materials surfaces.

2. Corrosion costs and economics

Corrosion costs society in three ways; viz, it is extremely expensive, it is extremely wasteful of natural resources at a time of increased concern over damage to the environment and it causes considerable inconvenience to human being and sometimes loss of life (Trethewey & Chamberlain, 1995; Ige, 2007). Corrosion is the greatest consumer of metals known to man. Corrosion of industrial metal is one of the oldest problems that have ever challenged the industrial world. Its cost is quite enormous and translates into billions of dollars in many developed nations. It is observed that calculations on a national scale are extremely difficult

and any figure produced for the annual cost of corrosion to a country cannot be considered precise. It can however be taken merely as an indication of the order of protection and prevention that have been added to the cost of deterioration due to corrosion (Ige, 2013). The sum of these costs is a measure of the total demands on the national annual cost of corrosion which varies from 1 - 3.5% of the GNP (Orman, 1976; Gasem, 2013; ASM, 2000). The figures obtained are only the direct economic costs of corrosion.

The indirect costs resulting from actual or possible corrosion are more difficult to evaluate but are probably even greater. It is estimated realistically to be around 300 billion dollars in United States of America (USA), while in developing countries like Nigeria it is assumed to be around 10 billion dollars and it is estimated to be around Rs 2.0 lakh crores per annum in India (Umoru, 2001; Natarajan, 2013). It must be noted that the high degrees of severity of corrosion leads to tremendous economic losses. Aside from its direct costs in monetary term, corrosion is a serious problem because it definitely contributes to the depletion of our natural resources. Also, the rapid industrialization of many countries indicates that there will be competition for metal resources and as such the price will increase (Fontana, 1987). It is observed that the effects of corrosion can be beneficial or deleterious. There are numerous effects of desirable application of corrosion which are available some of them are chemical machining, anodizing, etching, among others. However, the deleterious effects include; aesthetic deterioration, high maintenance and operating cost, plant shutdowns, product contamination, loss of valuable parts, effects on safety and reliability and the recent trend of product liability whereby the onus is on the manufacturers rather than the users. Although corrosion is inevitable, its cost can be considerably reduced (Jones, 1992; Orman, 1976; Fontana, 1987).

3. Mechanism of corrosion

Thermodynamic and electrochemistry are of great importance in understanding and controlling corrosion. Metallurgical factors frequently have a pronounced influence on corrosion resistance. Physical chemistry and its various disciplines are most useful for studying the mechanisms of corrosion reactions, the surface conditions of metals, and other basic properties (Fontana, 1987). As stated earlier, corrosion can be classified into three categories based on the mechanism of their reactions and these are; chemical, physical and electrochemical. Chemical corrosion is purely subjected to the basic laws of chemical kinetics of heterogeneous reactions and refers to cases of corrosion that are not accompanied by generation of electric current for instance, corrosion of metals in non-electrolytes or in dry gases (Koser, 1980). The attack on metal surfaces during etching is also an example of a corrosion process by chemical attack (Shreir, 1994).

The physical mechanism of corrosion is typified in the metallic corrosion of solid metals in contact with liquid metal. In most cases, the solid metal dissolves to form an alloy with the molten metal, while sometimes; attack on solid metal is due to penetration of the liquid metal into the grain boundaries of the solid metal (Umoru, 2001). Electrochemical reactions can be divided into anodic and cathodic reactions. While anodic reaction involves anodic dissolution,

at the cathode there is consumption of all the electrons released at the anode. It also depends on the environment and the cathodic reactions include: metal reduction, metal deposition, oxygen consumption, or hydrogen evolution. In some corrosion reactions the oxidation reaction occurs uniformly on the surface, while in other cases it is localized and occurs at specific areas.

3.1. Anti-corrosion coatings: Mechanism

There are so many mechanism of anti – corrosion coatings but generally, mechanism of coating can be differentiated into three, namely; barrier creation between substrate materials and environments, inhibition of the corrosion processes, and coating acting as sacrificial materials. However, recently one of the newest approaches is what is called “*active-passive*”. This involved the coating acting as barrier layers which will not allow permeation of corrosive agents to the metal surface (passive). While the active approach allows the formation of effective passive layer and this will impede the corrosion half reactions leading to Schottky barrier at the interface resulting in depletion of electrons (Dennis *et al.*2013).

4. Corrosion thermodynamics and kinetics

Corrosion science involves a study of electrochemistry, which are electrochemical processes that take place at electrodes. An electrode is essentially the boundary between a solid phase (metal) and a liquid phase (aqueous environment) and these processes take place across the phase boundary. The basic wet corrosion cell consists of four essential components, viz; anode, cathode, electrolyte and connections. The first law of corrosion control is regarded as the removal of any one of the four components of the simple wet corrosion cell and this will stop the corrosion reaction (Ige, 2007).

Corrosion in aqueous solutions has been found to involve electron or charge transfer. A change in electrochemical potential, or the electron activity, or availability on metal surface has profound effect on the rates of corrosion reactions. Thermodynamics give an understanding of the energy changes involved in the electrochemical reactions of corrosion. These energy changes provide the driving force and control the spontaneous direction for a chemical reaction. Thus, thermodynamics show how conditions may be adjusted to make corrosion impossible. When corrosion is possible thermodynamics cannot predict the rate, that is, corrosion may be fast or slow. It is postulated that in an electrochemical reaction, the most negative or active half-cell tends to be oxidized, and the most positive or noble half-cell tends to be reduced. Corrosion thermodynamics can also be used to state the criterion for corrosion. Corrosion will not occur unless the spontaneous direction of the reaction indicates metal oxidation (Umoru, 2001).

From an engineering point of view the major interest in corrosion is the kinetics or rate of corrosion. The principal aim for studying corrosion reaction kinetics are to develop empirical relationship that permit the prediction of corrosion rate under conditions that are different from those originally employed and to determine the mechanism of the overall process.

It is observed that corrosion is thermodynamically possible for most environmental conditions. Thus, it is of primary importance to know how fast corrosion occurs. Fortunately, most alloys corrode only slowly in many environments. Chemical kinetics is a study of the rates of such reactions. Corrosion in aqueous systems is governed primarily by electrochemical reactions and the understanding of the fundamental laws of electrochemical reaction kinetics is thus essential to develop more corrosion – resistant alloys and to improve methods of protection against corrosion (West, 1986). Electrochemical reactions either produce or consume electrons. Thus, the rate of electron flow to or from a reacting interface is a measure of reaction rate and electron flow is conveniently measured as current, I , in amperes.

4.1. Polarization

The rate of an electrochemical reaction is limited by various physical and chemical factors and the reaction are polarized or retarded by these factors. Polarization is defined as the displacement of electrode potential resulting from a net current. Its magnitude is frequently measured in terms of overvoltage. For cathodic polarization, electrons are supplied to the surface, and a buildup in the metal due to the slow reaction rate causes the surface potential, E , to become negative to e . Hence cathodic polarization is negative by definition. For anodic polarization, electrons are removed from the metal, a deficiency results in a positive potential change due to the slow liberation of electrons by the surface reaction, and anodic polarization must be positive. Most often, over potential is also used for polarization. Polarization is commonly classified into the following, viz; activation, concentration, resistance, and combined.

4.2. Anti-corrosion coating: Polarization

Chromium-based and zinc are used mostly as coating materials but due to stringent rules and regulations in terms of Health, Safety and Environment by many agencies, the former usage had declined progressively in the last decade. While the application of zinc as coating is discouraged significantly due to price fluctuation (Dennis *et al*, 2013). Hence alternative materials are sourced aggressively and one of such is the hybrid materials comprising of Unfunctionalised Graphene (UFG) and polyetherimides. This coating provide enhanced corrosion resistance to low alloy steel as depicted by data obtained from Tafel plot shown in Figure 1. It was also reported that the coating works on the active-passive mechanism of corrosion inhibition (Dennis *et al*, 2013).

The study of Wu *et al* (2010) showed that not all the materials evaluated possess corrosion resistance in a given environment. They deposited diamond-like carbon coating (DLC) on AZ31 magnesium alloy by ion beam deposition technique with Cr CrN acting as interlayers. Also evaluated was the effect of interlayers on the corrosion resistance of DLC on magnesium alloy. The results showed that the addition of Cr and CrN as interlayers improved the adhesion between coating and substrate effectively. The polarization result is presented in Figure 2 below. However it did not enhance the corrosion resistance of the DLC/magnesium alloy systems in 3.5 wt.% NaCl solution due to the formation of galvanic cell between substrate and interlayer in the region of through-thickness defects.

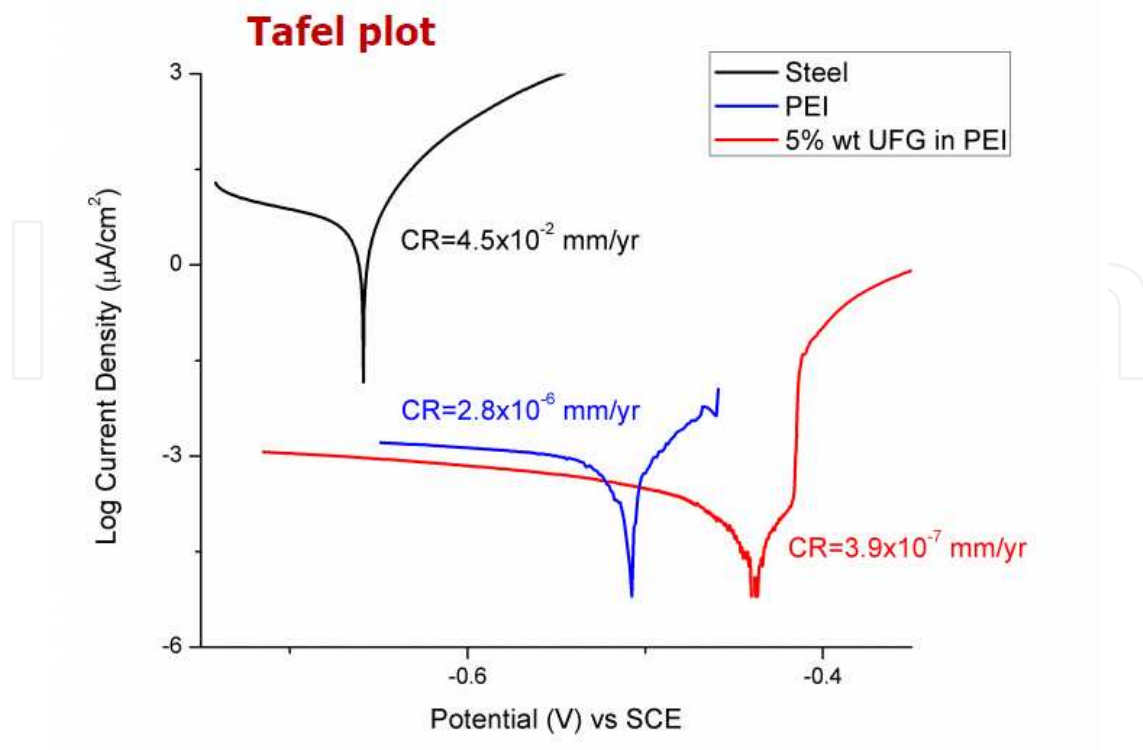


Figure 1. Tafel plot for uncoated and coated substrates (Dennis *et al.*, 2013)

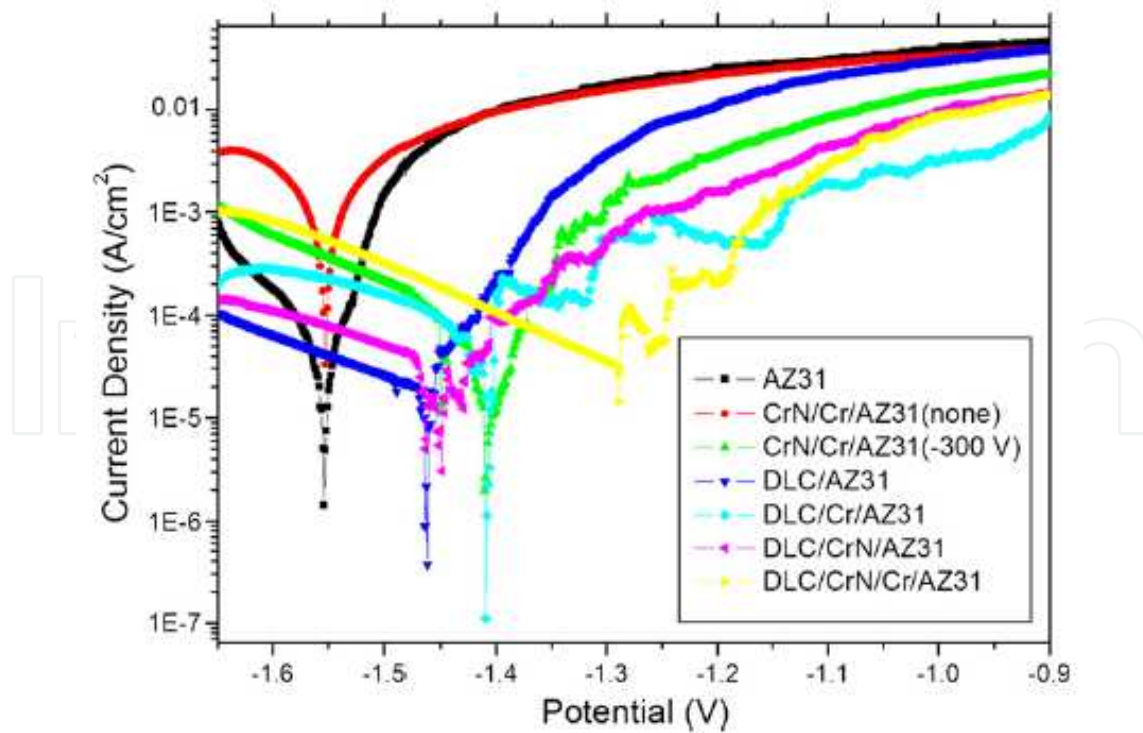


Figure 2. Polarization curves of all samples prepared in the study (Wu *et al.*, 2010)

4.3. Passivation

This is the loss of chemical reactivity experienced by certain metals and alloys under particular environmental conditions. The metals or alloys become inert and act as if they are noble metals such as platinum and gold. The following metals or alloys containing them show passivity; iron, nickel, silicon, chromium, and titanium, while zinc, cadmium, tin, uranium and thallium only show limited passivity under the conditions. Though passivity is difficult to define it is often described quantitatively by characterizing the behavior of metals, which show this unusual effect.

Figure 3 provides a method of defining passivity. A passive metal is one that demonstrates the typical S – shaped dissolution curve with exception of titanium, which does not possess a transpassive region.

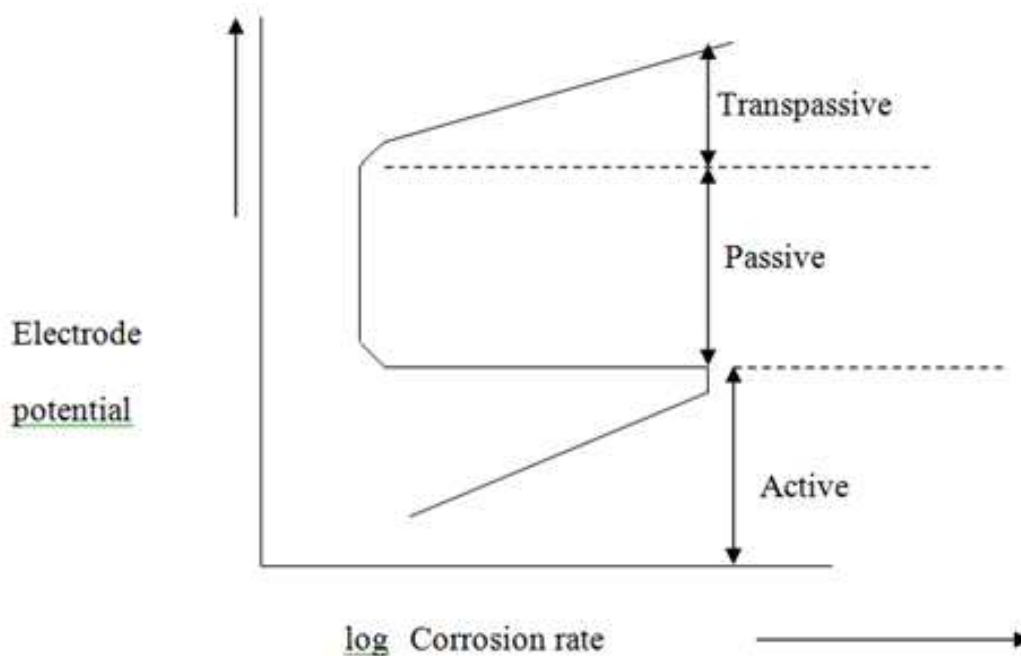


Figure 3. Corrosion characteristics of metal displaying passivity (Ige, 2007)

Passivity may be classified as anodic and chemical. *Anodic passivity* is when a metal is made an anode in an aqueous solution containing only anions with which it forms very sparingly soluble compounds. While *chemical passivity* is slightly more complicated wherein cathodic processes are involved on the same metals in corrosion – inhibitive solutions.

It may be considered as the action of corrosion products on the metal thereby influencing the reaction rate. The corrosion product rate is dependent on the solubility, structure, thickness, adhesion and so on. The film may be thin or thick; also it may be soluble or insoluble. In passivity, two conditions must be satisfied and they are; the redox potential of the solution must be more negative than passivity potential and the rate of the cathodic reaction must be greater than critical current density. Summarily, metals or alloys that possess an active-passive

transition become passive or very corrosion resistant in moderate to strongly oxidizing conditions; these materials lose their corrosion-resistance properties. These characteristics have been successfully used to develop new method of preventing corrosion and to predict corrosion resistance.

4.4. Passivation: Anti-corrosion coating

All the polarization resistance techniques (linear, potentiodynamic, cyclic and so on) can be employed to evaluate corrosion kinetics of coating systems; coupled with the coating thickness achievable in a given period. Current density is main parameter used to measure the efficiency of coating kinetics, the higher the current density the poorer the electrochemical behavior. High corrosion rates are characterized with a small passive range and lower pitting potential, suggesting the presence of defects and pores that allow the electrolyte diffusion, thus promoting the failure of the protective barrier (Castro *et al.*, 2005).

The aim of a research work carried out by Hashem (2004) was to prepare new monomer multi-silicon compounds which can acts as more durable adhesive and anticorrosion coating materials. The study also evaluated the structural mechanisms of their fragmentation in order to evaluate the reaction rate. The materials were identified by their retention times, number of cleavages and number of bonds. The results identified the isomers by the differences in the retention times. It was concluded that the isomers were organo-multi-silicon monomer compounds which performed creditably well as durable adhesive and anticorrosion coating materials. One of the rate determining factors in coating systems is the fall of polarization resistance R_p by its delamination with the formation of uniform double layer at the interface. This leads to filliform corrosion among others (Deen *et al.*, 2009).

5. Forms of corrosion

According to ASM (2000) there are basically three factors by which corrosion can be classified, viz; nature of the corrodent, mechanism of corrosion, and appearance of the corroded metal. The latter mode of classification is employed and this is due to the fact that it provides adequate information on the mode of failure associated with the corroded materials. The classification is based on the surface morphology (Figure 4 and Table 1) and it must be noted that the forms of corrosion are distinct in theory but practically, there are cases wherein the corrosion fits in more than one category. The corroded metals can be grouped into eight forms of wet (or aqueous) corrosion and these are (ASM, 2000): uniform or general corrosion, pitting corrosion, crevice corrosion, including corrosion under tubercles or deposits, filiform corrosion, and poultice corrosion, galvanic corrosion, erosion-corrosion, including cavitation erosion, and fretting corrosion, intergranular corrosion, including sensitization and exfoliation, dealloying, including dezincification, and environmentally assisted cracking, including stress cracking corrosion, corrosion fatigue, and hydrogen damage (Effird, 1993; Malka *et al.*, 2006; Barker *et al.*, 2012; Jiang, *et al.*, 2005; Ige, *et al.*, 2012; Colangelo and Heiser, 1974; Fontana, 1987; Chamberlain & Trethewey, 1995; Baker & Castle, 1993; Shreir, 1976).

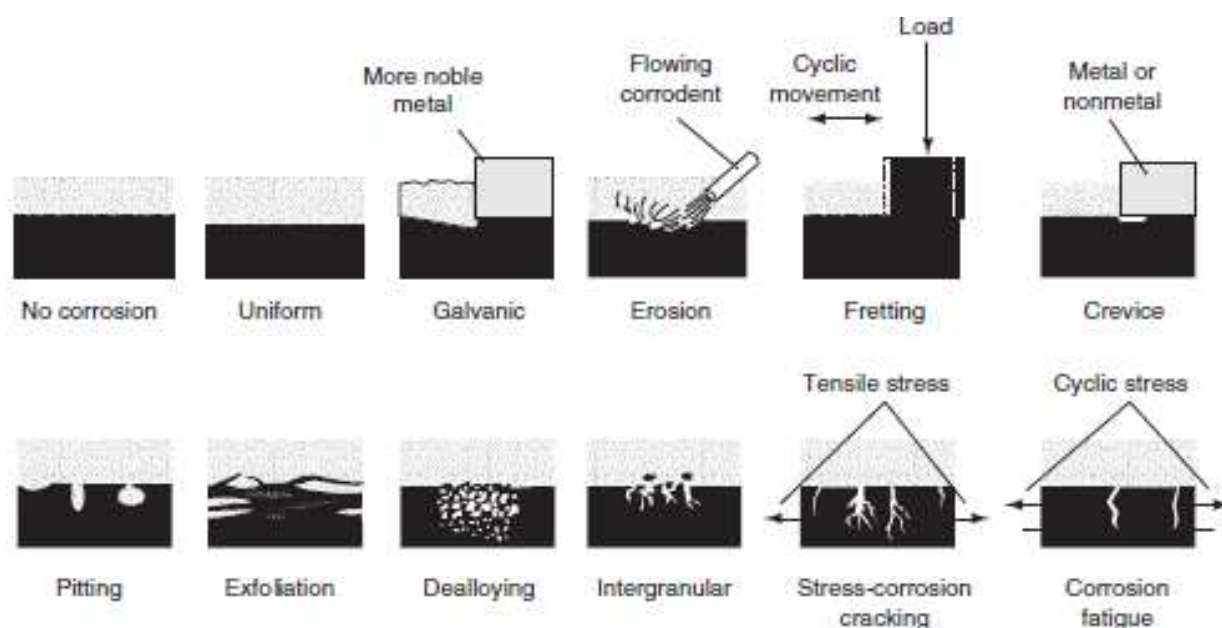


Figure 4. Schematic summary of the various forms of corrosion (ASM, 2000)

General Corrosion:	Localized Corrosion:	Metallurgical Influenced Corrosion:	Mechanically Assisted Degradation:	Environmentally Induced Cracking:
Corrosive attack dominated by uniform thinning	High rates of metal penetration at specific sites	Affected by alloy chemistry and heat treatment	Corrosion with a mechanical component	Cracking produced by corrosion, in the presence of stress
Atmospheric corrosion	Crevice corrosion	Intergranular corrosion	Erosion corrosion	Stress – Corrosion Cracking
Galvanic corrosion	Filiform corrosion	Dealloying corrosion	Fretting corrosion	Hydrogen Damage
Stray-current corrosion	Pitting corrosion		Cavitation and water drop impingement	Liquid metal embrittlement
General biological corrosion	Localized biological corrosion		Corrosion fatigue	Solid metal induced embrittlement
Molten salt corrosion				
Corrosion in liquid metals				
High – temperature corrosion				

Table 1. ASM classifications of corrosion types (Ref: Scully J R, Taylor D. W., Electrochemical Methods of Corrosion Testing, Metals Hand Book Vol 13, 1987)

6. Corrosion prevention and control

The fact that corrosion needs to be controlled cannot be overemphasized in view of the colossal amount of money that is expended on it annually. Materials are protected from corrosion through a wide variety of methods. In some measures, corrosion is avoided by careful choice of material and design of system so that the opportunity for corrosion of a certain specific sort does not arise. In most cases, the occurrence of corrosion is prevented or suppressed by the modification of the environment, modification of the materials properties, application of protective coatings and, cathodic and anodic protection. It must be appreciated that the choice of whether corrosion is to be avoided, suppressed or merely controlled depends on the economics of the processes involved (Ige, 2007). Hung *et al* (2011) highlighted the measures in preventing and control of corrosion as follows: materials selection, cathodic and anodic protection, and coating (Stack, 2002; Birks *et al.*, 1993; Reyes and Neville, 2001). However, it must be noted that the principles of corrosion prevention is based on modification of environments, electrochemical approaches, and corrosion resistant materials. The importance of coating cannot be emphasized because it encompasses all the corrosion control and prevention techniques such as cathodic protection (sacrificial), modification of environment (barrier effects and inhibition), and materials selection (development of corrosion resistant materials such as conducting polymers). The concept of coatings as its affect corrosion resistance is presented in the next section.

7. Coatings

According to Hegedus (2004), there are multi-layered systems in coatings which composed of primer and topcoat. The functions of each layer are specific but each layer is interactive. Coating materials can be metallic, inorganic or organic. Relatively thin coatings of *metallic and inorganic* materials can provide a satisfactory barrier between metal and its environment.

The chief function of such coating is to provide an effective barrier except for sacrificial coatings such as zinc. Metal coatings are applied by electrodeposition, flame spraying, cladding, and hot dipping and vapour deposition but inorganics are applied or formed by spraying, diffusion, or chemical conversion. Spraying is usually followed by baking or firing at elevated temperature. Metal coatings usually exhibit some formability whereas the inorganics are brittle and in both cases a complete barrier must be provided. Porosity or other defects can result in accelerated localized attack on the basic metal because of galvanic effects (www.metalsamples.com). Organic *coatings* involve a relatively thin barrier between substrate material and the environment. Paints, varnishes, lacquers, and similar coatings doubtless protect more metal on a tonnage basis than any other method for combating corrosion. Aside from proper application, the three main factors to consider for organic coatings are listed in order of importance as surface preparation, type of primer or priming coat and the selection of topcoat or coats.

Surface preparation is considered as one of the topmost factors in coating industry. It is known that if the metal surface is not properly prepared, the paint may peel off because of poor

bonding, If the primer does not have good adherence or is not compatible with the top coat, early failure occurs. If the first two factors are wrong, the system will fail regardless of the topcoat used. Poor paint performance is in most cases due to poor application and surface preparations. A tremendous variety of paints are available. Asphalt bituminous paints are often used on pipelines. Sometimes a cloth wrapping is used with the coating for reinforcement. Alkyds, glyptols, concrete, lead, iron oxide, phenolics, lithopones, titanium oxide paints and chlorinated rubber are just a few examples. Vinyl and epoxy paints have been widely adopted for corrosion application (www.corrosion-club.com).

There are many traditional techniques of coating and some of them are listed in Table 2 and shown in Figure 5. The techniques are thermal spraying, ion beam, immersion, welding, screen printing, dip-coating, electrogalvanising process, coating under vacuum, such as PVD (Physical Vapour Deposition), CVD (Chemical Vapour Deposition) among others (Wu *et al.*, 2010; metallic coated steel, 2013; ; Popoola *et al.*, 2012; Obadele *et al.*, 2011; Ochonogora *ET AL.*, 2012) and they are still commonly applied in coating metal substrates (Zhang & Tang, 2009). A typical example involved the use of cold tape coating system on new or reconditioned pipelines carrying oil, gas and water (Metallic coated steel, 2013). Their main function is to provide long term corrosion protection from underground elements as well as mechanical protection. The total tape system components consist of a primer applied directly to the pipe surface, an inner-wrap tape layer that provides a corrosion barrier and an outer-wrap tape layer that provides mechanical protection. The pipe coating process is done according to industry standards and some of them include DIN 30672, EN 12068, AWWA C-209, C-214 and C-225 (Figure 6). While Huang and Chen (2012) developed anti-corrosion tape which was effective on mild steel in marine splash zone. The mechanism of the developed tape coating was based on corrosion inhibition.

7.1. Anti – corrosion coating: Metallic materials

Metals and alloys are most commonly chosen for corrosion resistant concern, especially for metallic or ceramic substrates (Zhang and Tang, 2009). Due to serious environmental issues and health concerns, the use of chromating and phosphating phases (Bibber, 2007; Corell, 1998) are being replaced with molybdate, rare earth, silicate and titanium oxides or zirconium oxides (Oki, 2007; Phani *et al.*, 2005; Lunder, 2004; Song and Mansfeld, 2006; Montemora *et al.*, 2009; Wen *et al.*, 2008). For example, Huan and Buchheit (2004) studied a vanadate conversion coating and it was demonstrated that the coating formation offers increase corrosion resistance to pitting and suppress oxygen reduction reactions. However the vanadate coating has potentials of producing adverse health effects. While Guosheng *et al* (2013) concluded that Zn-Ni coating can serve as low potential cathodic coating for steel substrate and has a long life period and they meet the requirements for cathodic protection.

Metallic coated steel can be defined as a steel substrate coated with a layer of zinc, a zinc/aluminium alloy, a zinc/silicon alloy or pure aluminium. Typical coated steel is as illustrated in Figure 7 below. Fayomi and Popoola (2012) investigated the electrochemical behavior and the corrosion properties of Zn coating on steel substrates by means of Vickers microhardness

Applications	Techniques
Gas turbine components	Spraying
Electrolytic cathode for copper refinement	Thermal spraying
Water-cooled stator bars chips used in electrical generators	Chemical vapour deposition, physical vapour deposition
Semiconductor device and the liquid crystal device	Screen printing dip coating thermal spraying
Semiconductor processing equipment	Thermal spraying Sputtering Immersion Chemical vapour deposition, physical vapour deposition
Alkaline-containing environment	Spraying immersion roll coating
High temperature erosion-corrosion environments	Thermal spraying spray and fuse welding

Table 2. The Conventional Application Techniques for Making the Coatings (metallic coated steel, 2013)

and polarization measurements. While, the work of Durodola *et al.*, (2011) demonstrated that Zn coated steel plated performed creditably well in seawater or chloride containing marine environments compared with uncoated steel substrate. The sample concluded that the corrosion resistance of mild steel was improved after zinc deposition and that pitting corrosion observed can be attributed to ionic migrations which are influenced by the applied voltage.

7.1.1. Mechanism of corrosion protection offered by metallic coatings

Unarguably it is assumed that a metallic coating must be self-passivation and has a potential lower than that of the substrate. This allows the coating to have long life circle and high protecting efficiency (Short *et al.*, 1989). At the same time, the potential of coating materials should not be too negative; otherwise hydrogen embrittlement will happen to substrate. Generally, there are two basic mechanisms for metallic coating and they are: barrier effect, and cathodic protection. However a third approaches is by corrosion inhibition.

- **Barrier effect:** this involved the prevention of corrosion by isolation of the substrate from the corrosive environments. The isolation can be done physically by the presence of the coating or by the formation of corrosion products which provides a protective layer. Also surface passivation can occur due to formation of firmly bonded, hard and non-porous layer. The degree of passivation will depend on the acidity of the environment. The passivation of the surface of the coating will also affect its ability to provide sacrificial cathodic protection. For instance, the aluminium will be transformed into aluminium oxide, thereby creating a barrier that is non-porous, except in saline atmospheres (ABB, 2007; Krishnamurthy *et al.*, 2013; Wessling, 1999; Thiery ad Pommier, 2004; Hashem *et al.*, 2004; Bhadra

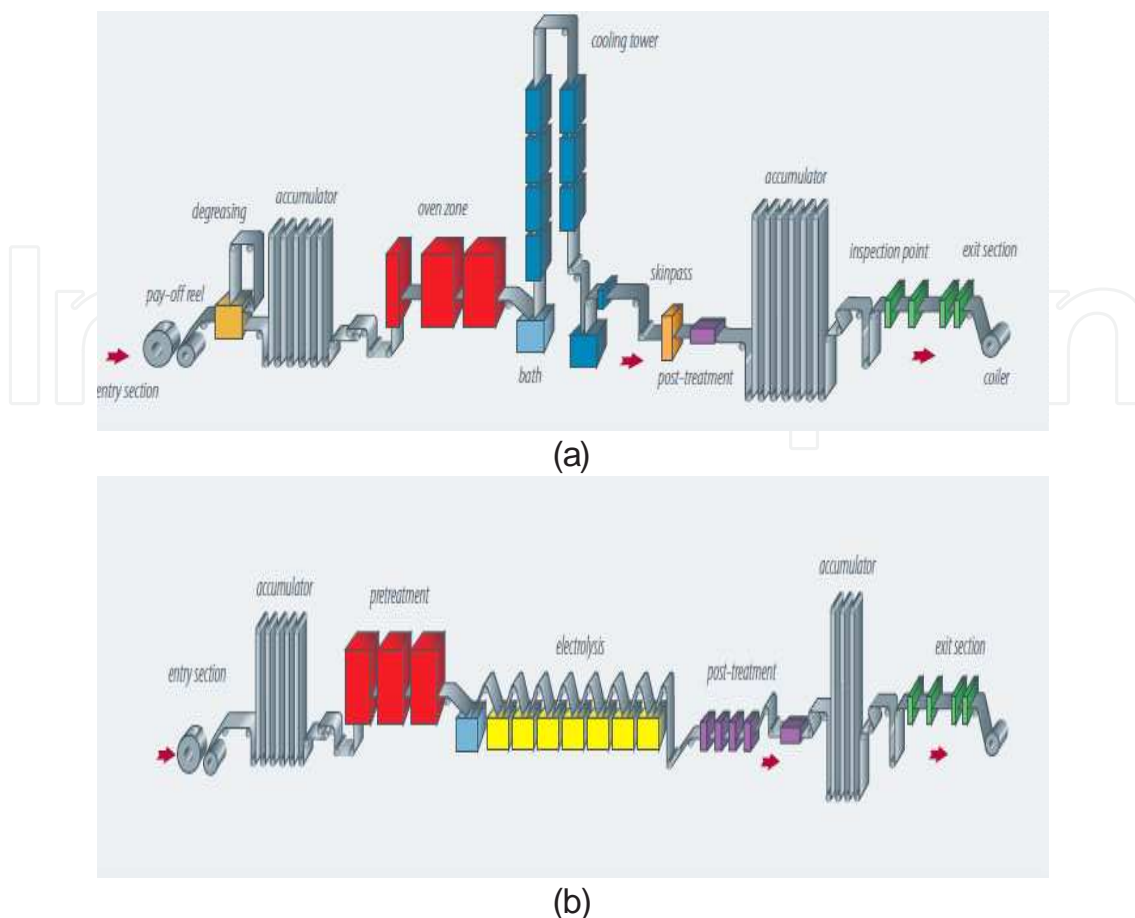


Figure 5. The hot dip coating process (a) and electrogalvanising coating (b) (Wu *et al.*, 2010)

et al., 2010). While Videla and Herrera (2009) stated that typical passivating agents for inhibiting microbial induced corrosion on metallic surfaces include inert metals, conductive polymers, and thiol-based monolayers.

- **Cathodic protection:** Corrosion is a phenomenon whereby an electrochemical cell is created consisting of an anode which is depleted to the benefit of a cathode. In practice, cells are formed as soon as a lack of surface uniformity appears, creating anode and cathode areas, whereby water acts as the electrolyte. In these cells, the steel will corrode every time it becomes the anode, but when it is the cathode, it will remain intact. The zinc and aluminium, which have a lower electrochemical potential than iron, will oxidise preferentially, thereby protecting the surface of the steel. The coating can therefore be considered to be inert with respect to the metal substrate, and will no longer be sacrificed. Hence, cathodic protection can be attributed to preferential dissolution of the metal substrates and this is due to mechanical damages (scratches, cut edges, holes etc) that may happen to the coating. This process is known as sacrificial protection. The sacrificial potential of a coating will depend on its corrosion products, which vary according to the type of metal in the coating. For example, zinc and other sacrificial coatings can protect steel from corrosive environments by cathodic protection (Mathiazhagan and Joseph (2011).

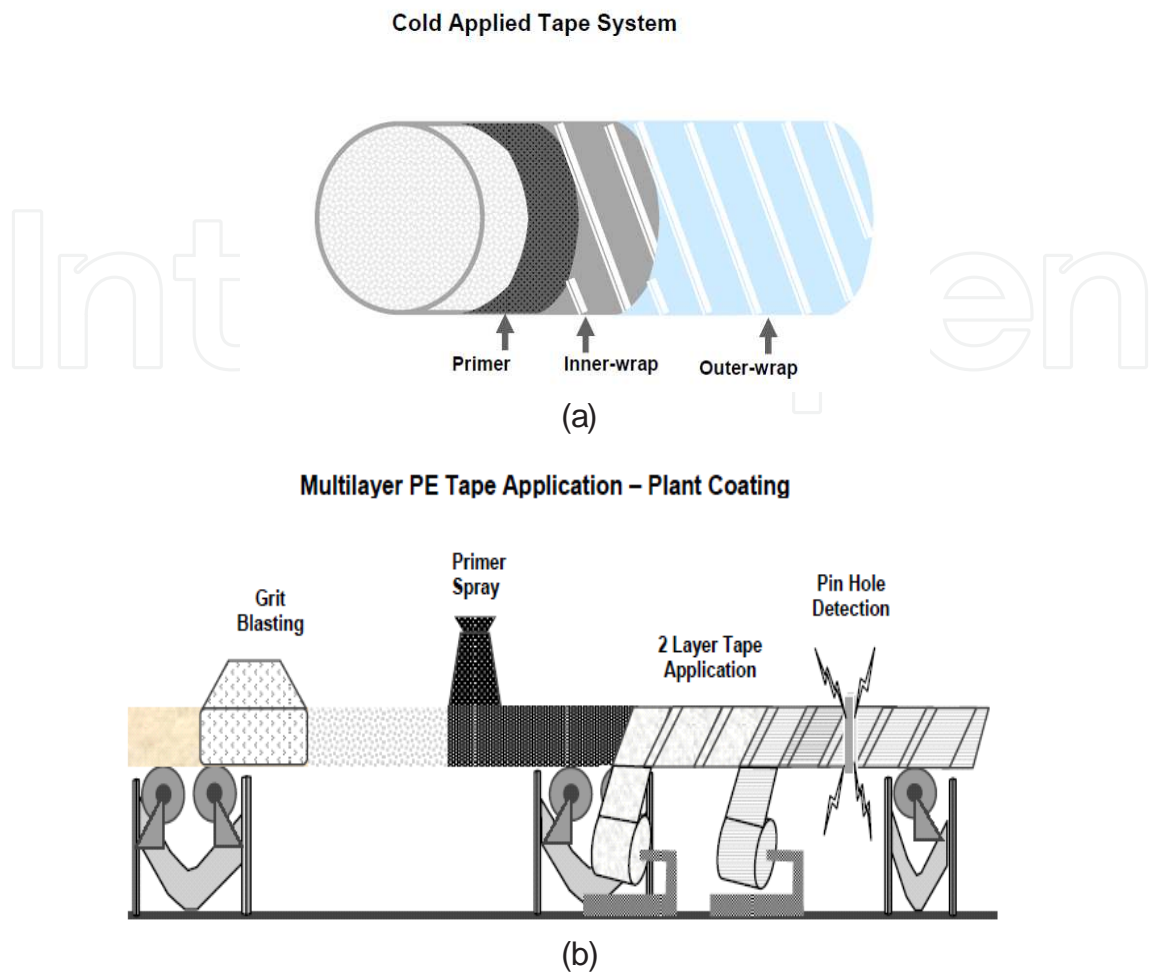


Figure 6. The cold tape coating system (a) and the pipe coating process (b) (Metallic coated steel, 2013)

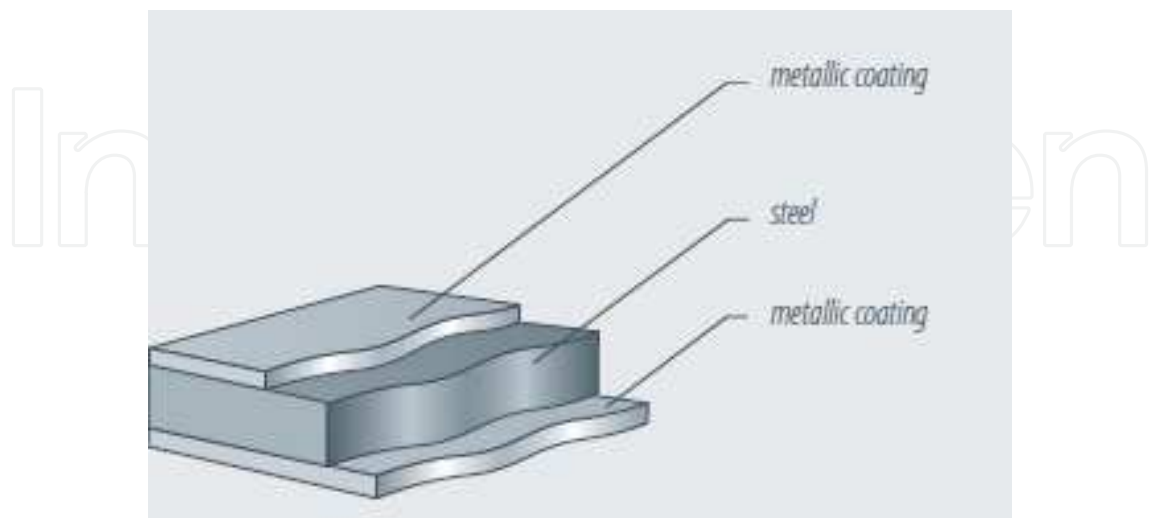


Figure 7. Typical coated steel (Metallic coated steel, 2013)

- **Inhibition:** The addition of inhibitors into coating systems are regarded as active corrosion protection as against passive corrosion protection as obtained by using barrier film mechanism. The inhibitor reservoir will act as an additional corrosion protection beyond the barrier protection offered by the oxide layer (Buchheit *et al.*, 2002). However the means of deploying the inhibitors are fuzzy and associated with economic and technical difficulties. One of the means of solving this issue is by production of self-healing coatings by integrating the active inhibiting compounds into existing convectional coatings (Shchukin *et al.*, 2006; 2007; Latnikova, 2012). Szabo *et al.*, (2011) showed that there are improved performances in the anti-corrosion property of coating systems inhibited by encapsulation in urea-formaldehyde resin.

7.2. Anti – corrosion coating: Ceramic materials

Several workers have used highly erosion-resistant ceramic coatings such as TiN, CrN in corrosive environments. They however realised that these ceramic materials are brittle and ultimately fail leading to catastrophe. They are very expensive and are used in critical applications; however, the use of novel metallic coatings is still under investigation (Wood and Hutton, 1990; Bousser *et al.*, 2008). Also, numerous patents have been obtained for ceramics materials in the formulation of coatings for anti-corrosion purposes. Some of the ceramics materials are used as corrosion resistant in different application such as: semiconductor industry, fuel cell, and corrosive water containing environments like gas turbine engines, heat exchangers and internal combustion engines among others (Iqhal *et al.*, 2005; Iqhal *et al.*, 2009; Hattori, 2008; Zhang and Tang, 2009).

Krishnamurthy *et al.* (2013) demonstrated the application of graphene as a passivating coating materials retards microbially-induced galvanic corrosion (MIC) of metals. The study was conceived on the basis that microbial fuel cell represents a galvanic cell and that the microbes will accelerates the metallic corrosion in the system. The experimental set up of the galvanic cell is shown in Figure 8. The study observed that graphene coating reduces considerably the MIC by preventing dissolution of soluble Ni and its performance is 10 – fold lower compared with uncoated anode (Figure 9). It was concluded that graphene coating have the advantage of possibility of being grown on large-area substrates by chemical vapour deposition.

Also that graphene coating prevents MIC by forming passivating layer which thereby restricted the movement of the solution to the Ni surface, disallowed the access of microbes to the Ni surface, and protect the Ni surface from microbes by product. With the aid of morphological study, Zaki and Abdul (2009) revealed that both nanostructured TiO₂ and TiO₂ demonstrated a little above average resistance to erosion-corrosion. Expectedly the nanostructured TiO₂ coating performed relatively better than convectional TiO₂ in slurry environment. This was achieved by reducing the gap between the splat boundaries and excluding secondary phase particles. They concluded that by reducing the volume of unmelted particles, number of pores, and provision of optimum surface topography there are possibility for improved performance by the coatings.

The application of talc as catalysts is well documented and it occurs naturally, also it can be synthesized by coprecipitation of divalent and trivalent cation salt solutions. This material was

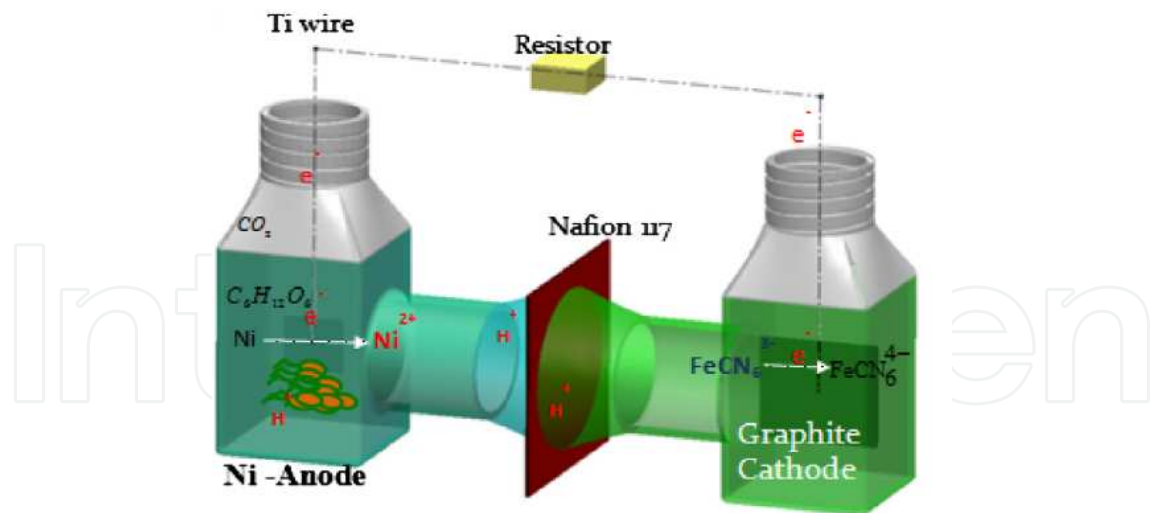


Figure 8. Schematic of a galvanic cell used in the study (Krishnamurthy *et al.*, 2013)

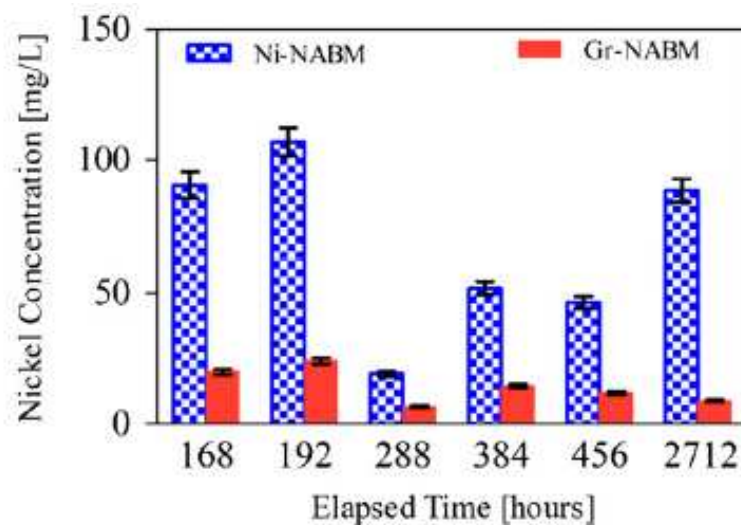


Figure 9. Soluble Ni (mg/L) in analyte of Ni – NABM and Gr – NABM (Krishnamurthy *et al.* 2013)

employed as coating in an aggressive environment and the results obtained revealed that it reduced the corrosion rates compared to uncoated surfaces. Post heat treatment increased the corrosion performance. It was also observed that it offers low toxic hazards and the method of production is quite simple. The suspected anticorrosion coating mechanism was due to formation of a barrier film on the substrates (Buchheit *et al.*, 1994).

7.3. Anti – corrosion coating: Polymeric materials

Zhang and Tang (2009) reviewed the patents that have been obtained in the area of polymeric materials as anti-corrosion coatings and they concluded that some polymers act as corrosion resistant materials due to the impervious nature of this material (Lee *et al.*, 2009; Kramer *et al.*, 2007). Wessling (1999) developed new anti-corrosion coating using the chemistry of

polyaniline (PAni), an Organic Metal (conductive polymer). The new Organic Metal polyaniline is almost regarded as a noble metal and it passivated metals by shifting their surface potential.

The usage of intrinsically conducting polymers (ICP) as anti-corrosion coating materials on metal surfaces have increased significantly in recent times. (Beck et al., 1994; Ahmed and MacDiarmid, 1996; Sitaram et al., 1997; Camalet et al., 1998; Martins et al., 2002; Tallman et al., 2002; Iroh et al., 2003; Tan and Blackwood, 2003; Zarras et al., 2003). Due to the ease of synthesis, tunable properties, low cost monomer and good thermal stability, polyaniline (PAni) is most applied of the available ICPs. (Genies et al., 1990, Gospodinova and Terlemezyan, 1998; Bhadra et al., 2009; 2011). Another advantage of the ICP is that it can be used as a single coat unlike other traditional materials that requires multi-layer coating before adequate protection of metal surfaces against corrosion can be achieved (Wessling, 1998). While Petersen (2006) evaluated the corrosion protection of anti-corrosive paint systems based on conducting polymers and the conducting polymers are polyaniline and polythophene. The study examined its application in four areas: shopprimers, ballast tank protection, protection in off-shore environment and protection of aluminium. Highlighted were the five possible protection mechanism for the conducting polymers and they are:

- Anodic protection and passivation of the substrate metal
- Formation of a protective metal/polymer complex
- Absorption of OH⁻ and inhibiting of cathodic disbondment
- Inhibition of the cathodic reactions
- Improve the conduction between zinc particles in zinc pigmented paints

Organic coatings are widely used as one of the corrosion protection and control methods for metals. It has vast applications in protection of porous refractory surfaces such as cement mortar or concrete structures. There are several factors that affect selection of suitable coating materials such as environmental factors and the nature of flow medium for pipeline systems. Organic polymeric materials are characterised by different functional groups. Some examples of organic polymeric materials are asphalt mastic and asphalt enamel, coal tar epoxy, extruded polyethylene, fusion bonded epoxy, multilayer polyolefin coating systems including polyethylene or polypropylene and polyurethane. For example, fusion bonded epoxy (FBE) have the following advantages which include: Saving in pipe thickness (or material), (ii) chemical inertness over a broad range of pH, presence of smooth and chemically inert surface, high friction resistance surface, ease in coating of complex shapes, ease in field welding, and ease in transportation of large size pipes and consequent saving in cost ((Vincent, 1999; Kellner *et al.*, 1998; Alexander, 1998) Malik *et al.*, 1999).

7.4. Anti – corrosion coating: Hybrid materials

Several attempts have been deployed to apply composite materials as coatings in the prevention of corrosion in various environments. Zhang and Tang (2009) highlighted the patents in anti-corrosion coatings area which include the work of Hazel *et al.* which provide improve

corrosion resistance for gas turbine components, such as the turbine blade as well as the turbine disk, shaft and seal (Suzuki and Watanabe 2007; Nagaraj and Hazel 2007; Buczek *et al.* 2009]. Composite materials allow the possibility of having versatile and wide ranging properties to be conferred on the coating materials. Some of the properties include: good adhesion characteristics, strain tolerance, self – healing characteristics, heat conductivity (Lee *et al.*, 2009; Kramer *et al.*, 2007; Dolan and Carson, 2007; Hill, 2009). It can also be due to other factors like technical or social factors and highlighted are two important factors.

Environmental Concerns: although chromate and phosphate phases have excellent corrosion resistance but due to restriction imposed by environment regulations in recent years, their applications as coating materials are progressively declined. Hence some environmental friendly compositions such as fluorometallate, vanadate among many others are investigated (Buchheit *et al.* 2006; Dolan and Carlson 2007; Mineyski *et al.*, 2006).

Economic consideration: apart from environmental factor, the economy of the coating is another important issue for consideration. As such, studied are currently being organised for cheaper and readily available materials (Hill, 2009; Kiksunov, 2007; Brady, 2006).

A study was carried out to investigate the effectiveness of a novel hybrid ceramic-polymer or creamer coatings on aluminium alloys in industrial atmospheric environments. The aim of the study was to elucidate information about the corrosion initiation mechanism and as well as determine the corrosion performance of the coated substrates in marine environments (Hihara and Kusada, 2011). SRI's anti-corrosion coating technology is based on preceramic polymers that have inorganic skeletons and organic side-groups. This means that at lower temperatures, the material behaves like a polymer: it can take the form of a liquid, can melt, and can form solutions. Then, it can be cured to crosslink at low temperatures to form non-meltable, non-soluble solids. At higher temperatures, it can be pyrolyzed and converted to a ceramic material. These formulations are inorganicorganic hybrids ("ceramers") in their nature reaching 80 to 90 wt% of inorganic content. Yet, the coatings can be designed to maintain hydrophobic characteristics (SRI, 2010). Hammer *et al.* (2012) determined the optimum concentration of TEOS and MPTS mixtures to be 8. The hybrid coatings were prepared by sol-gel techniques and the coatings were smooth, crack-free, adherent and optically transparent. The coatings present excellent corrosion protection efficiency and they are characterised with high breakdown potential and low current density even for high anodic potentials. The electrochemical data revealed that the coatings can performed exceptionally well in neutral saline and acidic environments.

Based on the work of Shi *et al* (2009), it was established that the presence of nanoparticles such as Si_2O , Zn, Fe_2O_3 greatly enhanced the anticorrosive performance as well as mechanical properties of epoxy coating. It was noted that SiO_2 nanoparticles is premised on barrier/passivation mechanism among others. Figure 10 illustrated the effects of corrosion rate on various coating systems on one hand and also as a function of chloride concentration on the other hand. Conclusively, the corrosion rate decreased as the chloride composition in the environment increased and also with the addition of various nanoparticles.

The new vista under study is the investigation of the synergy of various nanoparticles, their mechanism, and dynamics and kinetics in the coating system. Also the potentials of using the

nanoparticles as corrosion inhibitors for the anticorrosive properties of the coating system are under consideration (Lamaka *et al.*, 2007).

7.5. Anti – corrosion coating: New and emerging materials

Among new and emerging materials are nanomaterials, biomaterials, biomimetic and biodesign materials, microelectronic mechanical materials and smart materials, just to mention few. It is only smart and nanomaterials that are much interest in the coating industry and a comprehensive and aggressive research are currently being pursued. Some of the relevant studies are reviewed in this section.

Smart coating: It is estimated that 20% of the cost of corrosion in USA is accounted for by coating and allied industrial activities. This leads to the development of smart coating that can either reduces corrosion or predict the onset of corrosion in the system. The latter can be achieved by a simple strategy of change in colour stimuli. A smart coating is defined as any coating that changes material properties in response to an environmental stimulus and the changes can be preferably do so in a reversible manner (Meilunas, 2013). Some school of thoughts believed that terms such as responsive, adaptive, or active are more appropriate to describe these coatings because the coating does not undergo complex-thought process. The assumptions were that in as much as there are various stimulus/response, so also there are potential applications that can be engineered. Some smart coatings have been developed based on their light, temperature, humidity, pressure, electrical current, and many other properties. Smart coating can be differentiated into self-cleaning, self – healing, microcapsule healing, and anti – corrosion coatings.

Smart anti – corrosive coating is believed to be trigger off immediately corrosion commences in the system. A study investigated aluminum 2024 as the substrate for smart coating using sol – gel techniques to form a passive barrier. The coatings contain silicon, zirconium oxides and resin. A blend of polyelectrolytes was used as the sensor based on the pH of the system and in a neutral pH fluid; the polyelectrolyte/inhibitor blend is stable and won't lose its potency. A polyelectrolyte blend that was stable in acidic situations was mostly employed, but which quickly released its inhibitors in a basic environment. Generally, the coating system had strong adhesion to the aluminum substrate and was able to actively reverse the galvanic process at an emerging corrosion site (Meilunas, 2013).

The concept of self – healing anti-corrosion coatings was modelled after wound healing process (Figure 11). Improper wound treatment will leads to inflammation which can be likened to underlying corrosion in the coating systems, whereas wound disinfection can be likened to application of corrosion inhibitors. Introduction of corrosion inhibitors into coating systems for the purpose of self - healing can be achieved by various techniques which range from simple to complex methods. The techniques are limited by inhibitor solubility's, chemical costs, and technical difficulties such as manufacturing process (Latnikova, 2012). *Nanocoating:* Nanocoating is one of the recent trends in the application of nanotechnology in the prevention and control of corrosion protection and it is gaining momentum due to the fact that nanoscale materials have unique physical, chemical and physicochemical properties. Nanocoating involves the incorporation of nanoparticles in the coating formulation which enhance specific features (Mathiaghazan and Joseph, 2011).

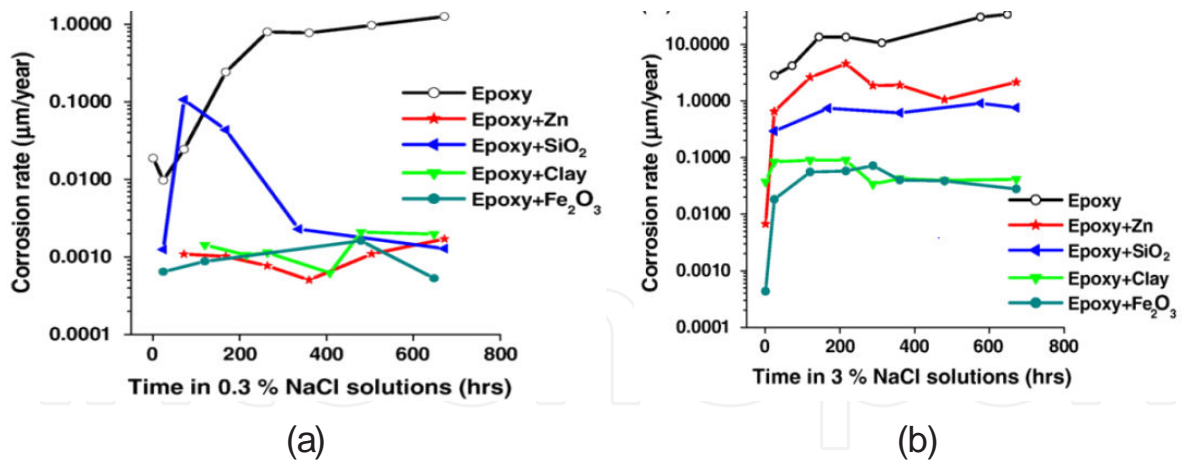


Figure 10. Temporal evolution of corrosion rate of epoxy-coated steel in (a) 0.3 wt.% NaCl solution, and (b) 3 wt.% NaCl solution, as a function of nanoparticles (Shi et al 2009)

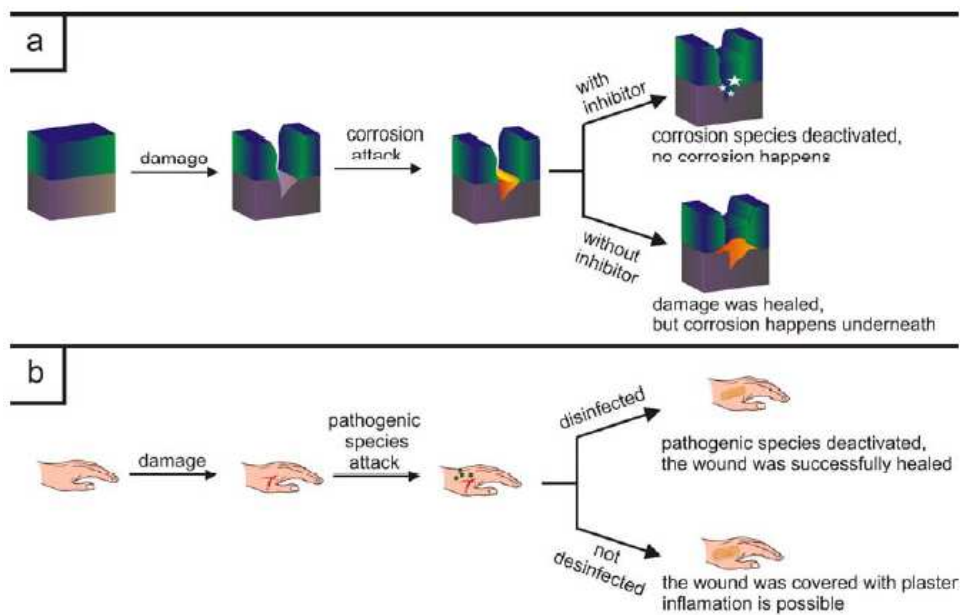


Figure 11. Bio-mimetic concept of self-healing process based on the combination of integrity restoration with application of corrosion inhibitors. (a) healing of a scratch on the surface of a metal substrate covered with anticorrosion coating. (b) healing of a wound (Latnikova, 2012)

Hung *et al* (2011) discussed the anticorrosive properties of non-conjugated polymer nanocomposites in the form of coatings having layered silicates. The results showed that the nanocomposites layered silicates have better corrosion protection compared to bulk polymers. This was obtained from corrosion data in terms of standard electrochemical corrosion measurements, including corrosion potential, polarization resistance, corrosion current, and impedance spectroscopy. While the Tafel plots and Nyquist plots are shown in Figure 12 and it was observed that as the concentration of the clay – nanocomposite increased the corrosion rate decreased. They attributed the performance to the diffusion and permeability characteristics of the O₂ and H₂O in the nanocomposites.

8. Conclusion

- Militating against corrosion is necessary in the industry because the penalties of failures due to corrosion can be very costly including safety hazards.
- Selective modification methods such as dipping, spraying, sol-gel, vapour deposition among others of metals and components is possible through the application of anti-corrosion coatings, therefore only the part which is at risk to degradation needs to be coated, leading to cost reduction as opposed to other traditional prevention methods
- Material loss and component failures can be prevented with proper selection of coatings/ materials in most manufacturing industries. Adequate knowledge of these processes is therefore inevitable.
- Anti-corrosive coatings produced new materials surfaces with numerous functional properties and unique features

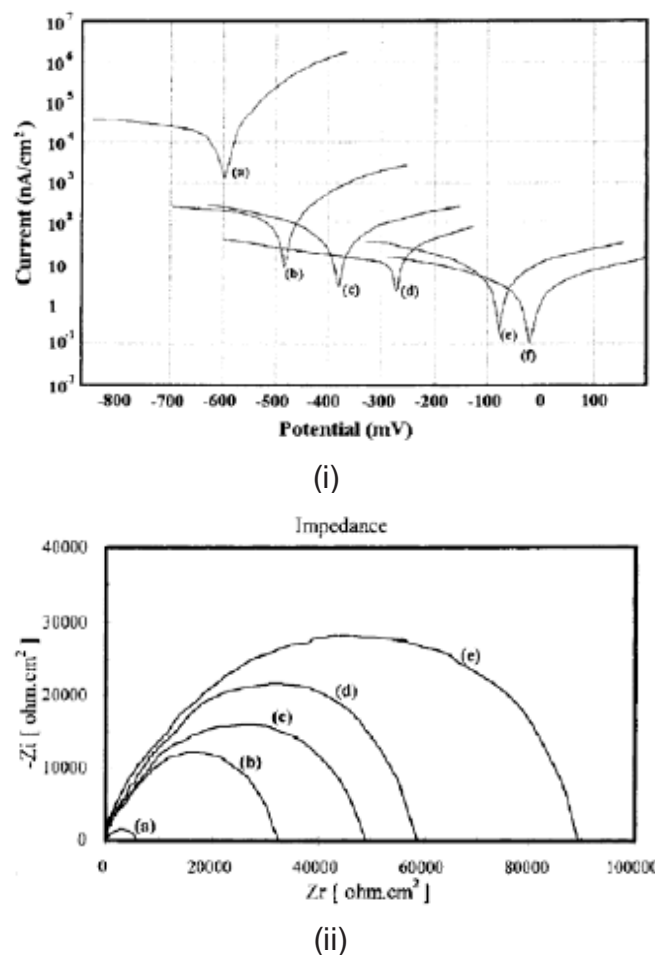


Figure 12. (i) Tafel and (ii) Nyquist plots of five CRS samples in 5 wt% NaCl aqueous solution (a) PMMA-coated, (b) CLMA1-coated, (c) CLMA3-coated, (d) CLMA5-coated, and (e) CLMA10-coated. (Hung et al., 2011)

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